Chapter 1. Introduction and outline of thesis

1.1 Background

Limestone is a natural resource defined as a calcareous material or rock with a calcium carbonate content of at least 70% (Oates 1998). Although there are extensive reserves of limestone worldwide, very few deposits are of sufficient quality to provide raw materials for specialised industrial applications and uses. Their commercial exploitation is dependent on the purity, homogeneity, colour and thickness of the deposit (Oates 1998).

From an industrial perspective, the term CaCO$_3$ of “high quality” includes two groups of substances, namely ground calcium carbonate (GCC) and synthetic or precipitated calcium carbonate (PCC). Ground calcium carbonate results directly from the exploitation of pure carbonate ore bodies and is a mechanically crushed, finely ground pure calcium carbonate product. PCC is synthesised via a chemical precipitation process (Mark et al. 1978). The advantage of PCC over GCC is that impurities from the limestone rock can be removed in the production process and the properties of the precipitated products can be controlled (Renaudin et al. 2008). The PCC products are therefore characterised by a higher degree of chemical purity, and by finer and more uniform particle sizes with narrower particle size distributions than GCC.

CaCO$_3$ has many uses in a wide variety of industrial and commercial applications. GCC is used for purposes such as manufacturing concrete or Portland cement, for producing lime to be used in, for example, soil stabilization and acid neutralization, for water treatment, and flue gas desulphurization (Oates 1998). Worldwide, PCC is mainly used as a filler and coating pigment in paper, plastics, paints, rubbers and adhesives. Other uses include manufacturing of glass, textiles, putties, chalks, sealant, inks, varnishes, food, cosmetics, chemicals and pharmaceuticals (Zhang et al. 2010; Windholz 1983). The variety of industrial applications requires that PCC is supplied commercially with various physical and chemical properties, among which are: chemical purity, particle size, specific surface area, density and morphology are of critical importance (Chakraborty & Bhatia 1996; Chakraborty et al. 1994; Tai & Chen 1998).
The world consumption of filler-grade CaCO$_3$ was 74 mega-tonnes in 2011, comprising of 60 mega-tonnes of ground (GCC) and 14 mega-tonnes of precipitated (PCC) material (Roskill 2012). Figure 1.1 shows the combined consumption (2011) and forecast demand (2016) for GCC and PCC by end users.

![Figure 1.1 World consumption (2011) and forecast demand (2016) for the GCC and PCC by end users (Roskill 2012)](image)

The South African lime industry differs significantly from the lime industries of the main industrialised countries where limestone deposits are widespread and of good quality. Only isolated deposits of high-grade limestone occur in South Africa (SA) (Mabuza et al. 2012). The principal use of limestone in SA is in the manufacture of cement, followed by metallurgical applications as a fluxing agent in steel making, the manufacture of lime, and agricultural uses. The use of PCC is limited to the paper industry and a fine-ground CaCO$_3$ (FGCC) of very high purity is used in the plastics, paint and rubber industries.

Idwala Carbonates (Idwala 2013), which is located near Port Shepstone (South Africa), produces FGCC by means of a limestone crushing and flotation process (Figure 1.2). This operation quarries a scarce, white, high purity calcitic and dolomitic limestone deposit. The production is energy-intensive, as it involves processes such as crushers, mills, and electric driers.
Speciality Minerals Inc. (SMI) is an international producer of high-quality minerals including PCC, GCC and lime (SMI 2013). A satellite PCC production facility (Figure 1.3), operated at Mondi Merebank by Speciality Minerals South Africa (SMSA), is the only dedicated PCC production plant in SA. The concept of satellite production facilities is used to implement research and development activities that are geared towards improving the quality of paper produced, as well as reducing cost. This is mainly achieved by improving the PCC properties, as well as increasing the percentage of PCC in the paper. This lowers the paper cost, but increases the amount of PCC used. SMI currently manufactures several customized PCC products using proprietary processes. It starts the production of lime from high-quality limestone sources. In the case of SA, Speciality Minerals imports high-quality quicklime (CaO) as feedstock for their PCC production plant (SMI 2013).
On industrial scale, high-grade limestone rock is currently the preferred raw material for the production of both PCC and GCC. However, the replacement of this natural raw mineral as feedstock by calcium-rich, waste-derived products in the manufacture of PCC may contribute towards a more sustainable use of a country’s natural resources. The conversion of such solid wastes into PCC via industrial mineral carbonation can therefore represent a potentially-viable strategy for the re-exploitation of industrial wastes, but it can also contribute towards the mitigation of carbon dioxide emissions since industrial mineral carbonation could make use of industrial CO$_2$ streams as feedstocks.

The Council for Scientific and Industrial Research (CSIR, Pretoria, SA) has developed a novel technological process for the conversion of waste gypsum (CaSO$_4$·2H$_2$O) into high-value elemental sulphur with a low-grade CaCO$_3$ being generated as a by-product (Maree 2005). The technology has been patented in several countries under the following title: *Conversion of a sulphur-containing waste material into a sulphur-containing product*. The multi-step process (Figure 1.4) of sulphur recovery can be described as follows (Mbhele et al. 2009; Nengovhela et al. 2007):

- Thermal reduction (900 to 1100°C) of waste gypsum to produce calcium sulphide (CaS) using reducing agents, including solid carbon materials such as coal or activated carbon (Eq. (1.1)) (Kato et al. 2012; Ma et al. 2011; Mihara et al. 2008; Nengovhela et al. 2007), carbon monoxide gas (Eq. (1.2)) (Miao et al. 2012; Zhang et al. 2012; Tian & Guo 2009; Li & Zhuang 1999), or hydrogen gas (Eq. (1.3)) (Ning et al. 2011):

$$\text{CaSO}_4 (s) + 2\text{C} (s) \rightarrow \text{CaS} (s) + 2\text{CO}_2 (g) \quad (1.1)$$

$$\text{CaSO}_4 (s) + 4\text{CO} (g) \rightarrow \text{CaS} (s) + 4\text{CO}_2 (g) \quad (1.2)$$

$$\text{CaSO}_4 (s) + 4\text{H}_2 (g) \rightarrow \text{CaS} (s) + 4\text{H}_2\text{O} (l) \quad (1.3)$$
• Direct aqueous carbonation of CaS to produce hydrogen sulphide (H$_2$S), and low-grade CaCO$_3$ as a by-product. The reaction proceeds according to equation (1.4).

\[
\text{CaS (s) + H}_2\text{O + CO}_2\text{ (g) \rightarrow H}_2\text{S (g) + CaCO}_3\text{ (s)} \quad \Delta H_{25^\circ C} = -37.7 \text{ kJ}
\] (1.4)

• Recovery of elemental sulphur from H$_2$S via the commercially available, chemical catalytic Claus process (Mark et al. 1978)

Figure 1.4 Elemental sulphur production from waste gypsum. (the area highlighted in red delineates the part of the process where low-grade CaCO$_3$ is produced, and represents the focus of this study)

CaS is an intermediate product generated in the first step of the process. Although the conversion of CaS into H$_2$S has been studied (Brooks & Lynn 1997; Nishev & Pelovski 1993; Biswas et al. 1976), little, if any, effort has been given to the controlled production of commercial-grade CaCO$_3$ during the second step of the process.

1.2 Hypothesis and statement of originality

The commercial technology for producing PCC in an aqueous medium using Ca(OH)$_2$ as the calcium source (Eq. (1.5)) (the Ca(OH)$_2$-H$_2$O-CO$_2$ reaction system) is used on industrial scale (Souto et al. 2008), but the carbonation of alkaline waste materials requires processes other than those used for the carbonation of a Ca(OH)$_2$ slurry.

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\text{Ca(OH)}_2\text{ (s) + CO}_2\text{ (g) \rightarrow CaCO}_3\text{ (s) + H}_2\text{O (l)}
\] (1.5)
The research hypothesis is that high-grade PCC (product containing greater than 99 mass% as CaCO₃) with variable physicochemical properties (morphology and particle characteristics, including particle size, surface area and density) can be produced from waste gypsum (CaSO₄·2H₂O) via the intermediate CaS product (Eq. (1.4)) in a mineral carbonation process by controlling operating parameters and conditions during the calcium carbonation step (Figure 1.4, highlighted area).

This study, therefore, focused on the production of high-grade PCC in a sulphide medium, using calcium sulphide (CaS) as the calcium source in the CaS-H₂O-CO₂ reaction system. A one-step, direct aqueous mineral carbonation (Eq. (1.4)) and a two-step, indirect mineral carbonation process route was used. For the indirect mineral carbonation process, CaS dissolution was induced by either CO₂ (Eq. (1.6)) or H₂S (Eq. (1.7)); this step was followed by the precipitation of solubilized calcium (Eq. (1.8)) in a separate reactor.

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\begin{align*}
2\text{CaS} (s) + \text{H}_2\text{O} (l) + \text{CO}_2 (g) & \rightarrow \text{Ca(HS)}_2 (aq) + \text{CaCO}_3 (s) \quad (1.6) \\
\text{CaS} (s) + \text{H}_2\text{O} (l) + \text{H}_2\text{S} (g) & \rightarrow \text{Ca(HS)}_2 (aq) + \text{H}_2\text{O} (l) \quad (1.7) \\
\text{Ca(HS)}_2 (aq) + \text{H}_2\text{O} (l) + \text{CO}_2 (g) & \rightarrow \text{CaCO}_3 (s) + 2\text{H}_2\text{S} (g) \quad (1.8)
\end{align*}
\]

1.3 Objectives

The objective of this project was to study a process that could be used for the production of high-quality PCC from CaS, the intermediate product of a waste gypsum treatment process, as the starting material (area highlighted in Figure 1.4). The experimental focus was on the control of the crystallization process during the carbonation stage to produce high quality CaCO₃ particles with specific physical properties. Specific areas of interest were the:

- chemical purity of the carbonate product;
- physical properties of the products (particle size, morphology or shape, density, surface area, porosity and crystallinity);
- minimization of additional chemical requirements and overall energy input into the carbonation reaction; and
- minimum production of wastes or by-products.
The specific objectives were:

- To produce PCC, and via a Claus process, elemental sulphur from waste gypsum
- To assess process conditions controlling the end-product quality (direct vs indirect mineral carbonation reaction using CO₂).

The use of industrial gypsum wastes as primary material, replacing mined limestone for the production of PCC would not only alleviate gypsum waste disposal problems, but would also convert significant volumes of this waste material into marketable commodities. The purity and crystal structure of the carbonate products determine their market value and, therefore, the proposed mineral carbonation process of waste products will control the characteristics of the final product.

1.4 Thesis outline/overview

To contextualise the study, a general background is given in Chapter 1 regarding the industrial and commercial applications of natural and synthetic CaCO₃. An overview of the South African lime industry is given together with a brief discussion on the CSIR’s waste gypsum treatment process. The hypothesis, statement of originality and objectives of the study are formulated.

A literature overview on PCC is given in Chapter 2. The existing PCC production routes as well as the use of industrial solid wastes as alternative feedstocks for PCC production are discussed. The application of PCC is determined by a number of strictly defined parameters and therefore the effect of process conditions on the physicochemical properties of PCC is also included in the literature review.

Chapter 3 contains a detailed description of all the experimental and analytical methods used during this study. This is followed by two chapters containing experimental results. Chapter 4 describes the direct aqueous CaS carbonation (one-step) process and experimental results pertaining to the characteristics of CaS in the presence of CO₂ in the CaS-H₂O-CO₂ system.

Chapter 5 describes the indirect (or two-step) process for the production of high-purity CaCO₃. The thesis is consolidated with overall conclusions, and recommendations are made for aspects meriting further investigation (Chapter 6) Appendix A contains a list of experimental equipment and range of experimental uncertainties. Appendix B lists the test matrix that was followed.
1.5 **Originality of this work**

The study focused on the production of precipitated calcium carbonate from industrial gypsum wastes. Precipitated calcium carbonate is normally produced by contacting CO$_2$ with lime (Ca(OH)$_2$). This study focused on the following new and innovative approaches for the formation and characterization of precipitated calcium carbonate:

- Waste gypsum is used as raw material.
- Two configurations were studied. In the first configuration, CaCO$_3$ contaminated with coal impurities was produced. A second configuration was proposed as an improvement to the first configuration which made the production of a chemically pure CaCO$_3$ possible. Another original input was to identify the conditions needed to manipulate the morphology.

**References**


